

#### TAYLOR

The Constants Involved in Calorimetric

Combustions Making use of Sodium

Peroxide and Potassium Chlorate as the

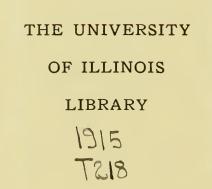
Medium for the Supply of Oxygen

Chemistry

M. S.

1915







UNINESSAY DE RECORDA

# THE CONSTANTS INVOLVED IN CALORIMETRIC COMBUSTIONS MAKING USE OF SODIUM PEROXIDE AND POTASSIUM CHLORATE AS THE MEDIUM FOR THE SUPPLY OF OXYGEN

BY

SCOTT CHAMPLIN TAYLOR

B. S. University of Illinois, 1913

#### THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

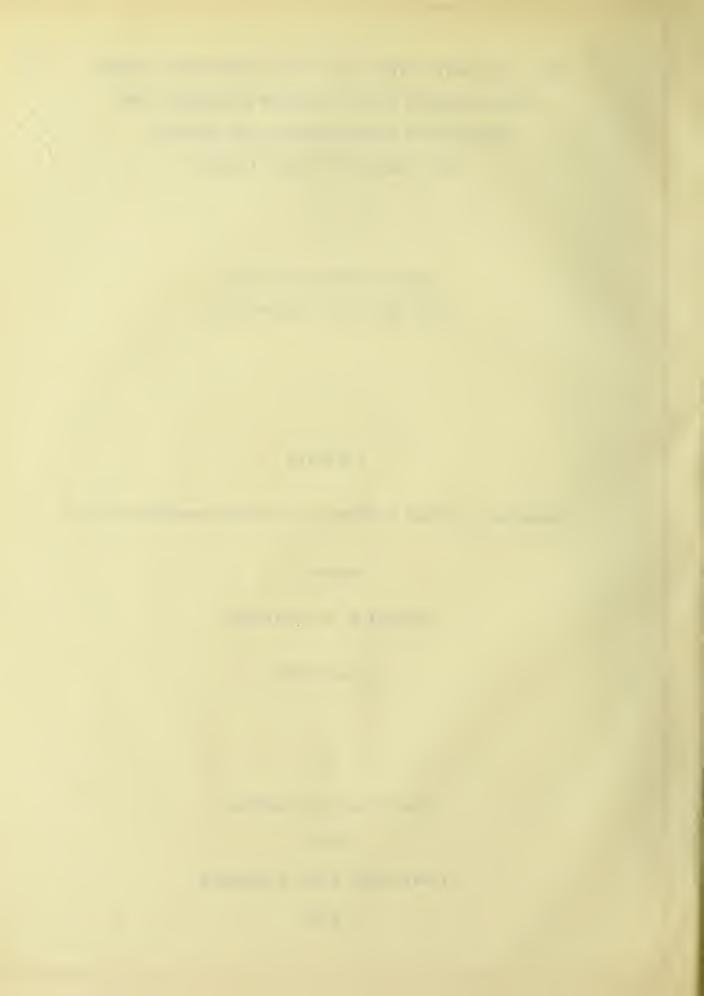
IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1915



ME

### UNIVERSITY OF ILLINOIS THE GRADUATE SCHOOL

June 1, 1915

1 HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-				
VISION BY Scott Champlin Taylor				
ENTITLED THE CONSTANTS INVOLVED IN CALO	RIMETRIC COMBUSTIONS			
MAKING USE OF SODIUM PEROXIDE AND POTASSIUM CHLORATE AS THE MEDIUM FOR THE SUPPLY OF OXYGEN BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE				
DEGREE OF MASTER OF SCIENCE IN CHEMISTRY  In Charge of Thesis  W. A. Word  Head of Department				
Recommendation concurred in:*				
	Committee on Final Examination*			
	Thur Diamination			

<sup>\*</sup>Required for doctor's degree but not for master's.

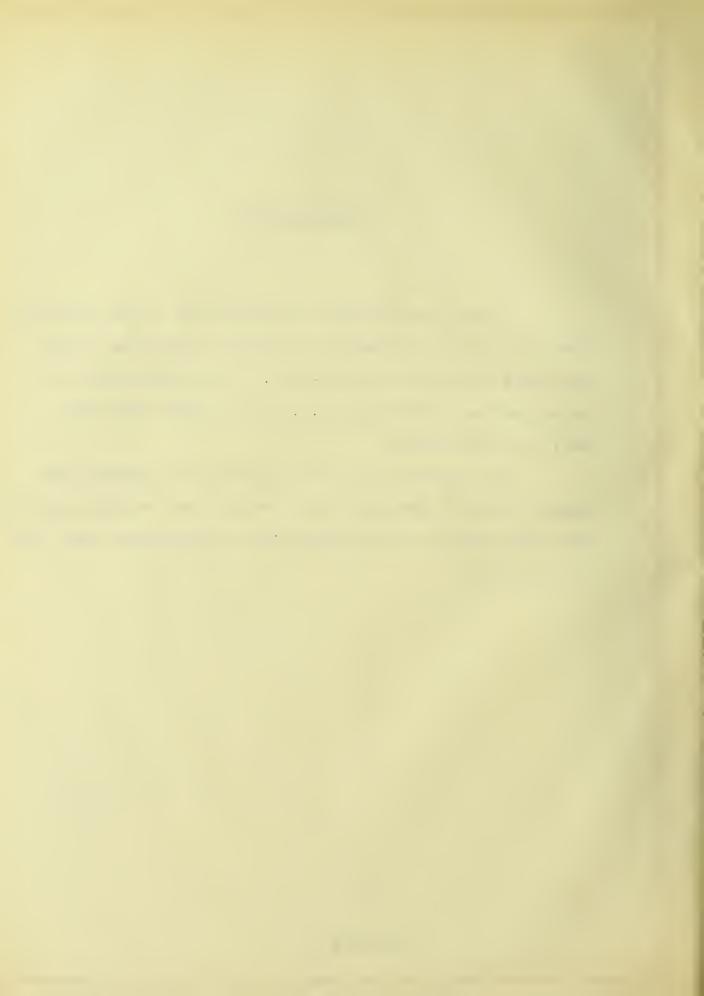
Digitized by the Internet Archive in 2013

1715 Tal8

#### ACKNOWLEDGMENT

This investigation was carried out in the Chemical Laboratory of the University of Illinois during the collegiate years 1913-1914 and 1914-1915. It was undertaken at the suggestion of Professor S.W.Parr and was carried out under his supervision.

The writer takes this opportunity to express his sincere thanks to Professor Parr for the very valuable assistance and direction so willingly given in connection with this investigation.



#### CONTENTS

	Pages
INTRODUCTION	1
Historical	1
Purpose of Investigation	2
Outline of Present Investigation	5
EXPERIMENTAL	6
Choice of Standard Substance	6
Apparatus	13
Heat Value of Potassium Chlor- ate	15
Reactions for Potassium Chlor-ate	15
Hydration Factor for Sodium Benzoate	21
SUMMARY	22

and the second second

100

- 4.0 0 .......

11 -- 12111 -----

A comment of the same of

IN . AT INVEN

## THE CONSTANTS INVOLVED IN CALORIMETRIC COMBUSTIONS MAKING USE OF SODIUM PEROXIDE AND POTASSIUM CHLORATE AS THE MEDIUM FOR THE SUPPLY OF OXYGEN

#### INTRODUCTION

#### Historical

The use of sodium peroxide as a means for combustion in calorimetric work was first described in 1900.\* The essential part

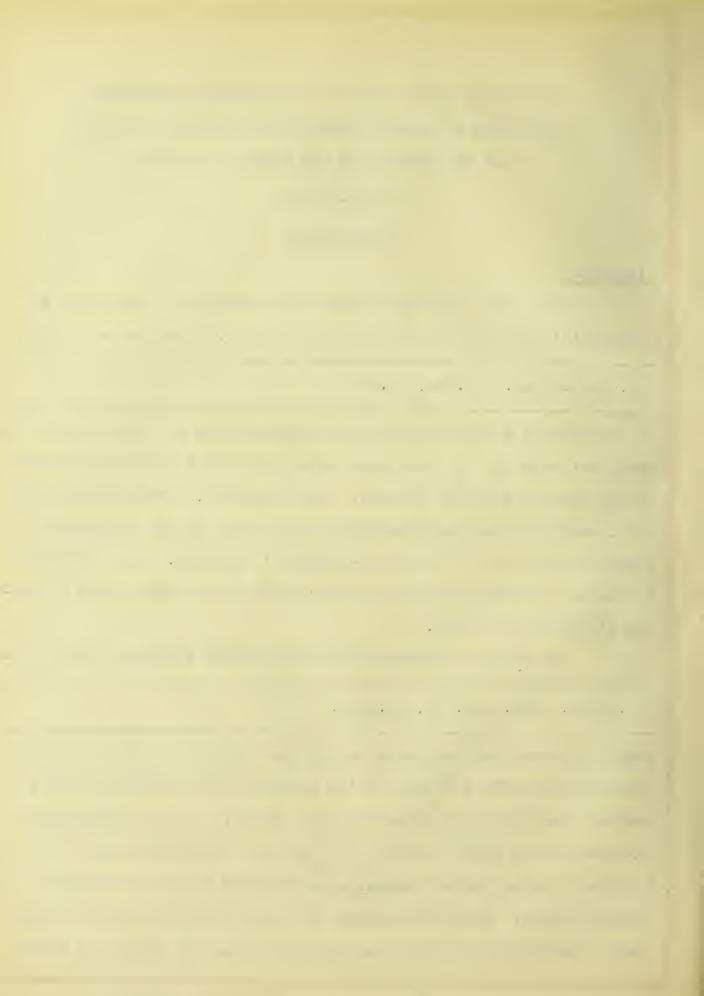
\* J. Amer. Chem. Soc. 22, pp.646.

of the process as outlined was the determination of the ratio of the true heat value of the substance burned and the total heat evolved by the reactions in the process. This constant, seventy-three per cent, was determined empirically by comparison of the results obtained by the use of the Mahler-Atwater instrument. This constant is the same whether the excess heat is due to the absorption of carbon dioxide or of water.

In further experiments, \* using widely different fuels, in-

complete combustion was noted and by the addition of other chemicals the oxidizing effect of the sodium peroxide was increased so that a complete combustion was generally the result. Of the accelerators examined, those which proved to be the most effective were: (a) a mixture of potassium and ammonium persulphate and (b) potassium chlorate alone. These substances of course required an additional heat correction due to their heat of reaction, the amount of which

<sup>\*</sup> J. Amer. Chem. Soc. 29, pp.1606.



was determined.

but little used. A difficulty is present in any mixture on account of the necessity of absolutely even distribution of the ingredients. Also since one of the components, potassium persulphate, is not always of the same percentage purity the ultimate mixture requires standardization for each lot made. The changes in the heat value of different lots of accelerator, even though small, are apt to be confusing, for the average user is unable to see why the correction should not be the same for each lot.

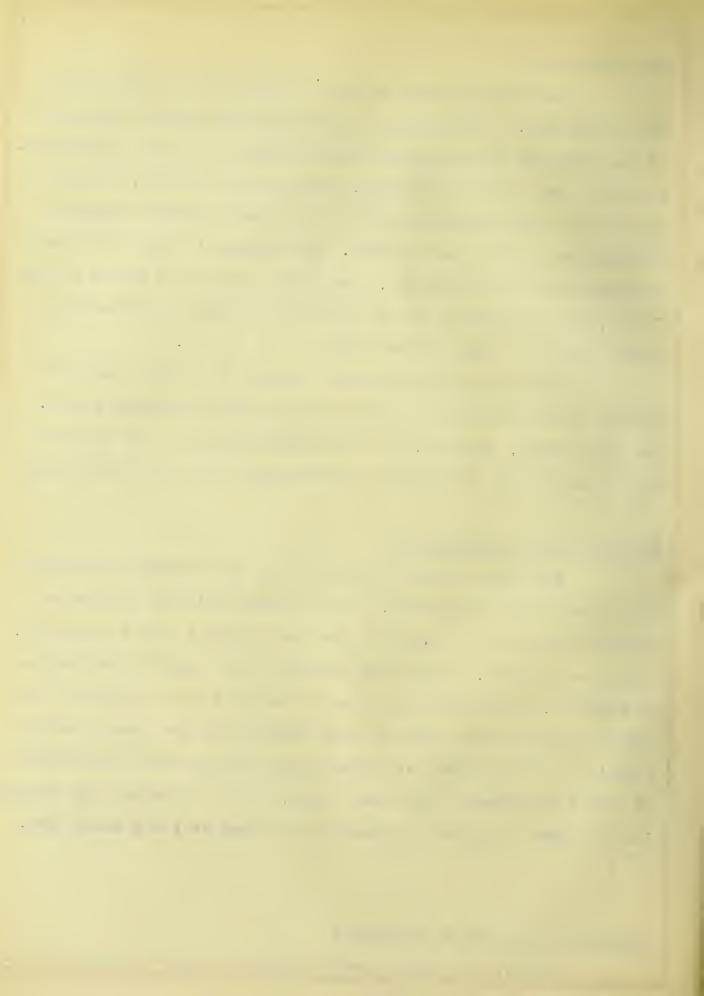
Potassium chlorate on the contrary is a pure substance equally effective for most coals and now almost universally used. Its heat factor, moreover, is relatively smaller and its behavior in the reaction seemingly more constant than the other accelerator.

#### Purpose of the Investigation

For these reasons and because of the numerous advantages in the new form of apparatus, it has seemed desirable to make an extended study of the reactions involved together with an analysis, so far as possible, of the heat factors of the various components. In addition, mention might be made of the fact that the use of this form of apparatus has grown to such proportions that every feature relating to the accuracy or reliability of the results obtained is of utmost importance to its many users. It is estimated that approximately 1500 of these instruments are in use at the present time.

#### Changes in the Form of Instrument

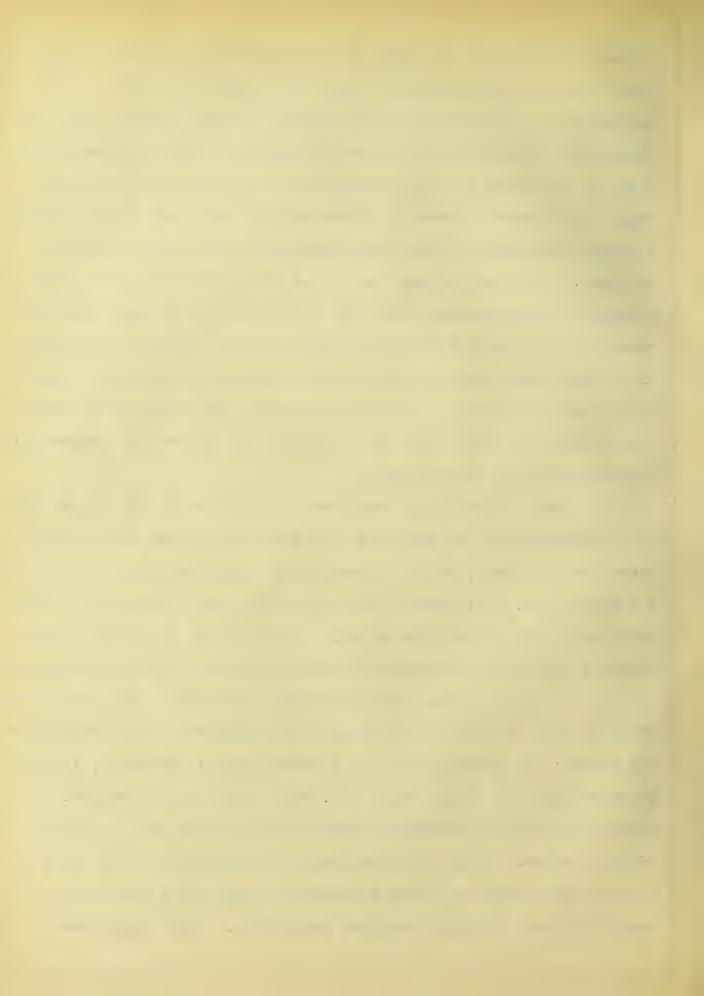
One of the objectionable features of the old style of in-



strument and perhaps the cause of the occasional appearance of unburnt carbon was the fact that the fused mass in the bomb is surrounded by the metal which is in contact with the water. With this instrument, upon opening the bomb, a portion of the contents would cling to the walls of the instrument and on analysis of the same would show traces of unburnt carbon and in every case would contain a larger percentage of this constituent than any other portion of the mass. This was perhaps due to the fact that that part of the mixture in direct contact with the cold walls of the bomb does not reach a sufficiently high temperature to cause complete combustion or if this temperature is reached the contents are cooled so rapidly by the metal being in direct contact with the surrounding water that a sufficient time does not intervene for all of the combustible constituents to burn completely.

Now in devising a new form of apparatus it was argued that if the contents of the bomb are so insulated from the surrounding water that the heat, which is generated during the initial period of the combustion, is retained within the fused mass, instead of being radiated to the surrounding water, it will result in a higher temperature which will consequently result in a more complete combustion.

A new form has been constructed, therefore, with the above facts in mind and tends to overcome this imperfection in the following manner: By referring to the accompanying illustration, it will be noted that the fusion cup (2AC), which contains the charge, is separated from the surrounding water and the outer bell (1AC) by a thin air space. With this arrangement a large part of the heat, which is generated, is retained within the bomb for a sufficient length of time to afford complete combustion. This arrangement



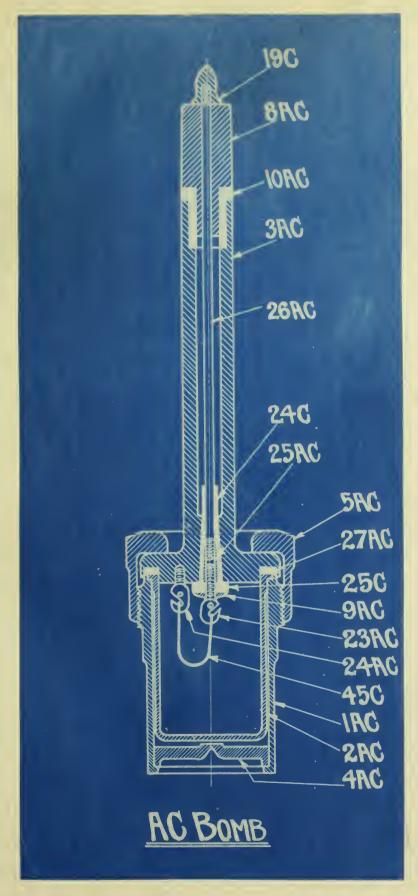
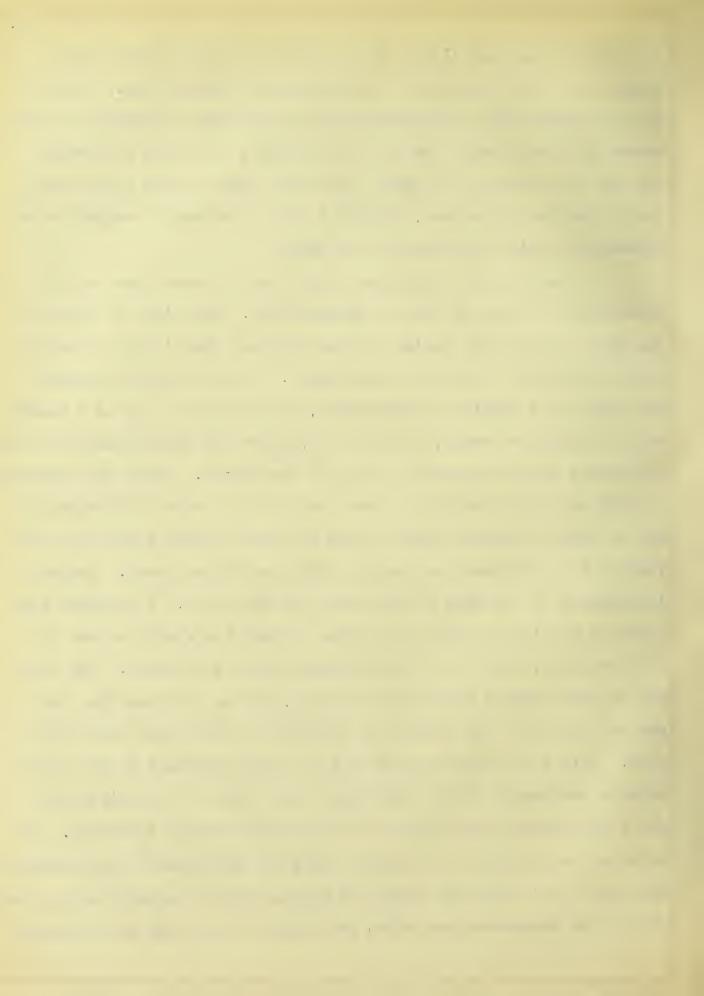


Fig.1

L DE L DE accomplishes another object very essential in calorimetric work; namely, that the heat shall be extracted in a short time. As soon as the combustion is completed and the instrument commences to cool, water is drawn through the holes in the bell up to the hot fusion cup and by occupying the space, from which the air has been forced out by the heat generated, affords a direct medium of conduction and subsequent rapid extraction of the heat.

Among other advantages might also be noted those which come under the head of ease of manipulation. The first of these is the small size of the fusion cup and the fact that it can be easily removed from the rest of the instrument. In this way the operator can remove the complete contents and, by placing the cup in a beaker with a little hot water, is able to dissolve the fused mass with less difficulty than with the old style of instrument. While the contents of this cup are dissolving, a new charge for a second determination may be made in another cup; so with one extra fusion cup we have in reality two instruments at only a slight additional cost. Another improvement is the ease of attaching the fuse wire. The method consists in passing one end of the wire through the eyelet of one of the terminals, (24AC) so it will extend beyond the eyelet. The free end is then wrapped around the terminal binding in place the free end of the wire. The process is repeated for the other end of the wire. This little improvement will be gladly welcomed by the users of this instrument for it simplifies this part of the manipulation and also assures a good contact of the wire with the terminals. Of no minor importance is the change which has been made in the wrenches. The top of the bell just below the cap and the cap as well are in the form of an octahedron and these two parts fit into the two wrenches



provided for the purpose. With this arrangement a better hold is obtained than with the old style of wranch.

#### Outline of Present Investigation

The present investigation consists of a series of calorimetric determinations varying the several constituents one by one in such a manner as seems advisable for the best study of the heat sources of the various components.



#### EXPERIMENTAL

#### Choice of Standard Combustible Substance

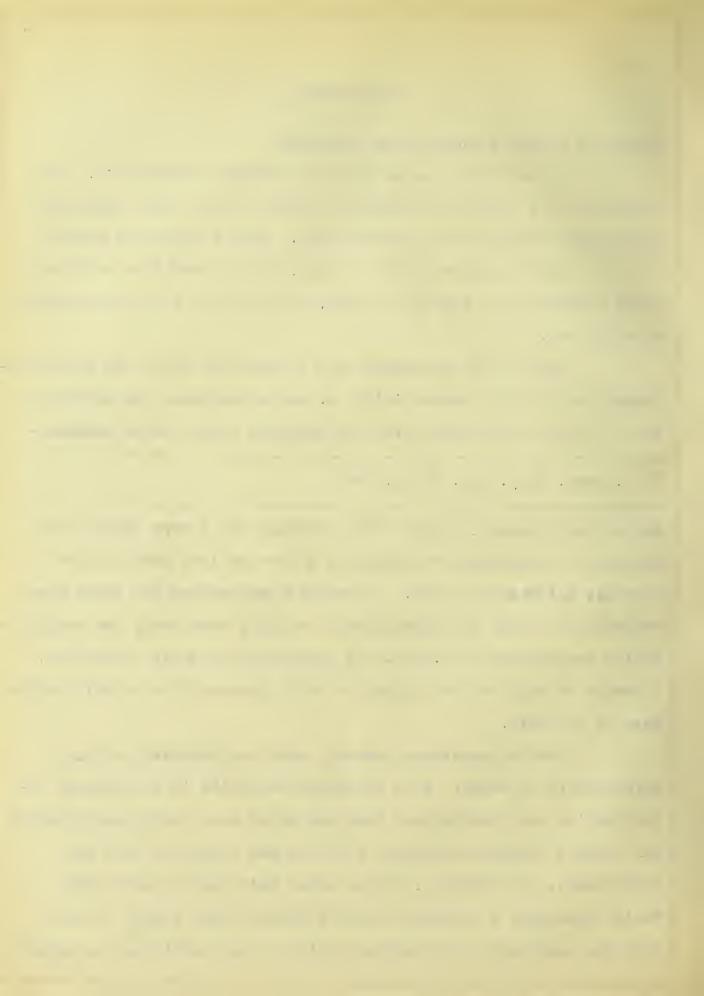
In work which deals with calorimetric combustions, the selection of a suitable standard substance is the first important thing which confronts the investigator. Such a substance should have two chief characteristics; namely, (a) It should be capable of being prepared in a very pure state, and (b) it must burn completely when ignited.

One of the substances used in previous work\* and which conformed to the first prerequisite, as above outlined, was naphthalene. In this work which covers an extended series using naphthale

\* J. Amer. Chem. Soc. 29 pp.1606.

ene as the standard, results were obtained which were fairly concordant but occasional variation of a more or less erratic sort were now and then met with. A probable explanation for these discrepancies is that the naphthalene, having a relatively low volatilization temperature (217.68°C.) is volatilized without combustion. Attempts to vary the conditions so as to prevent this volatilization were of no avail.

Another substance commonly used for standardization of calorimeters is sugar. This substance was tried in the present investigation and results were obtained which were fairly satisfactory but certain features connected with the use seemed to call for improvement. For example, it was noted that the contents after fusion presented a somewhat porous property which seemed to show that the heat during the initial period is not sufficient to cause a



completely molten condition of the contents. A remedy suggested itself in the form of an increased charge which would bring the mass up to the fusion point. This furnished a better fusion and more concordant results. This procedure has a number of good points and is worthy of more extended examination.

Another substance used in the work referred to\* and one which gave fairly good results was benzoic acid. In the present

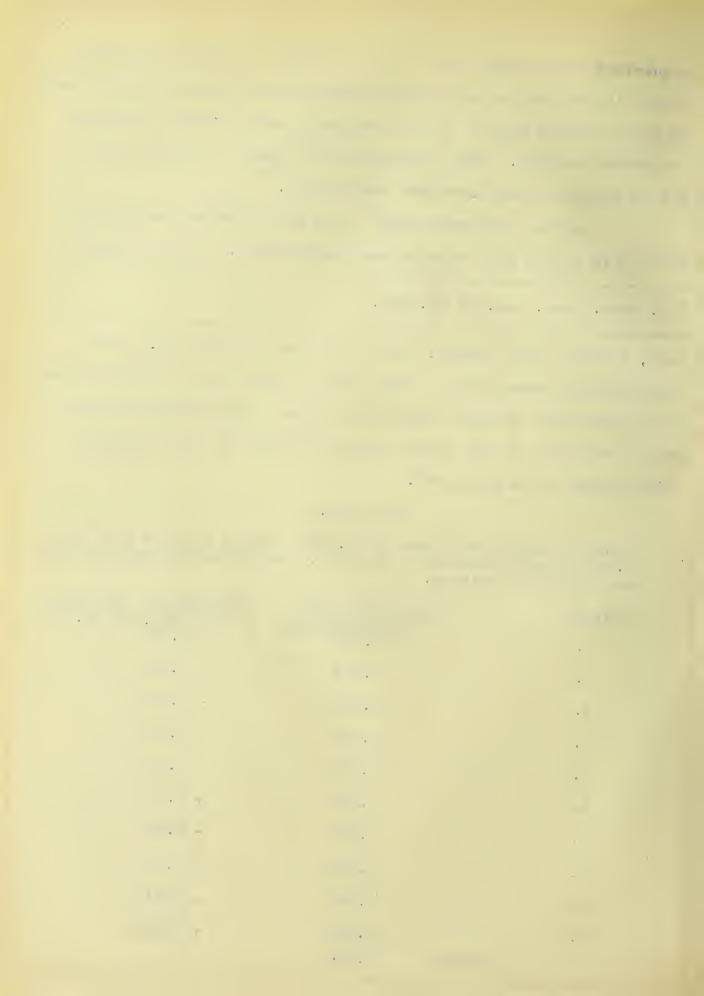
work, however, the results, which are shown in Table No.1, were occasionally inconsistent. This might be due to the volatilization of the substance without combustion, or to a reaction between the sodium peroxide and the benzoic acid; the heat of said reaction being wholly or in part lost.

#### Table No.1

Showing Temperature Rise for 0.5000 gram of benzoic acid and 1.0000 gram of Potassium Chlorate. Determination made as soon as charge was made up.

Test No.	Temp	erature Rise	Differences from mean
1.		in degrees cc. 2.274	in degrees cc.
2.		2.270	- 0.014
3.		2.272	- 0.012
4.		2.282	- 0.002
5.		2.274	- 0.010
6.		2.296	+ 0.012
7.		2.289	+ 0.005
8.		2.275	- 0.009
9.		2.296	+ 0.012
10.		2.321	+ 0.037
	Average	2.284	

<sup>\*</sup> J. Amer. Chem. Soc. 29 pp.1606.



That a preceeding reaction does take place between the benzoic acid and the sodium peroxide seems very probable because of the acidic property of the former and the basic character of the latter and this is substantiated by the following experiment. Two sets of bombs of two each were made up in the usual manner (i.e. 0.5000 gram of benzoic acid, 1.0000 gram potassium chlorate and 10 grams of sodium peroxide). One set was placed on the steam bath for about twelve hours and the other kept at room temperature for the same period of time. Without opening, these bombs were ignited in the usual manner and the temperature rises noted; the results of which with the average from Table No.1 are given in Table No.2.

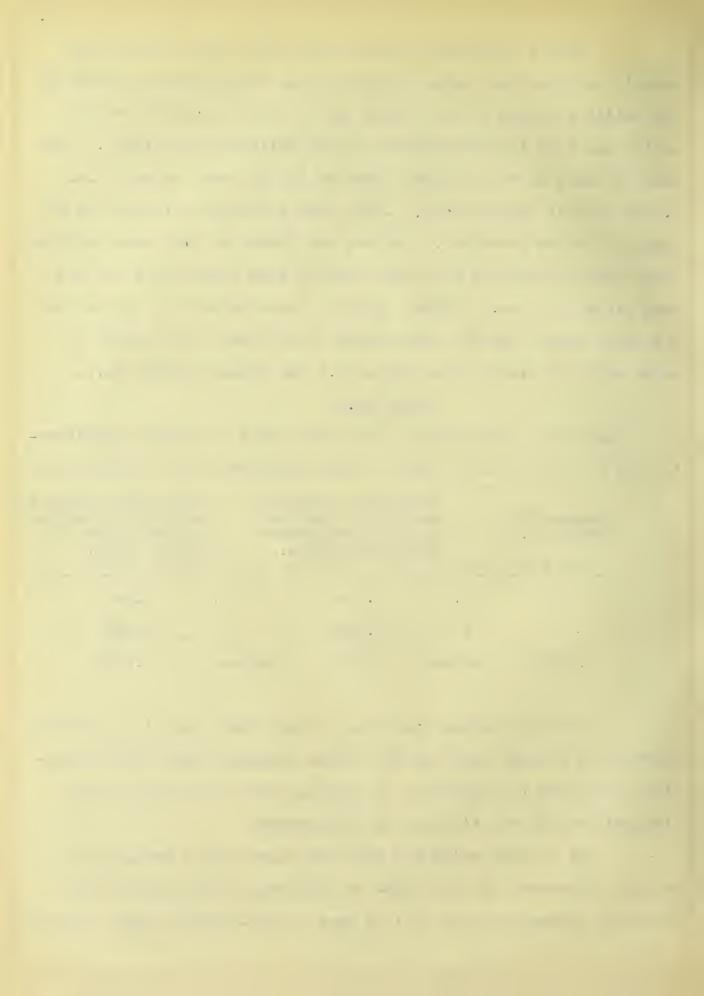
#### Table No.2

Comparison of Temperature Rises when Bomb is ignited immediately and after twelve hours at room temperature and on steam bath

Average from Table No.1	Bom at	perature Ris b after stan Room Tempera twelve hour	ding Bon ture on	perature Ris b after star Steam Bath : lve hours.	nding
	1.	2.266	1.	2.240	
	2.	2.275	2	2.226	
2.284°C.	Average	2.270	Average	2.233	

These determinations seem to show that there is a reaction between the benzoic acid and the sodium peroxide under these conditions, and that this reaction is variable but in the main is influenced both by the time and the temperature.

Up to this point the work has shown that a standard combustible substance for this type of instrument must have the two following characteristics: (a) It must be non-volatile under the con-



dition accompanying the reaction, and (b) It must not form any preliminary reactions with the components of the charge.

Since sodium benzoate is the resulting product from the reaction between benzoic acid and sodium oxide, it would seem obvious that it would answer to the latter of these prerequisites. It would then remain to be shown by experiment if it will satisfy the former.

To test the fulfillment of these prerequisites, the following experiment was performed. Charges consisting of the following compounds were made up and the charge ignited in the usual manner: 0.7500 gram of sodium benzoate, 1.0000 gram of potassium chlorate and 10 grams of sodium peroxide.

Table No.3

Showing the Temperature Rises obtained for the above charge

Test No.		Temperature Rise in degrees centigrade
1.		2.762
2.		2.753
3.		2.756
4.		2.761
5.		2.753
6.		2.752
7.		2.753
8.		2.754
	Average	2.755

The uniformity of these results seem to show that this substance, sodium benzoate, possesses the two necessary properties as above outlined. To further test the behavior of this material,

<sup>\*</sup> Kahlbaum's Preparation.



it was determined to make a similar experiment with all components the same except the standard substance and to use the standard amount of 0.5000 gram. It is often the case in the reaction between chemical substances that the proportional amounts of the constituents has a great influence on the reaction taking place and a substance for this work should react the same no matter what are the relative proportions of each constituent.

#### Table No.4

Showing the Temperature Rise for 0.5000 grams C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>Na, 1.0000 gram KClO<sub>3</sub> and 10 grams Na<sub>2</sub>O<sub>2</sub>.

Test	No.	Temperature R degrees cent	
	1.	1.884	
	2.	1.882	
		Average 1.883	

It is now interesting to compare the results obtained in Tables No. 3 and 4.

Assuming that  $0.153^{\circ}\mathrm{C.}$ , the correction adopted from other experiments for the  $\mathrm{KClO}_3$  and fuse wire, is correct\* and subtracting

\* Directions for Using the Parr Standard Calorimeter (new form)p.12

this from each average rise as shown in Tables No.3 and 4, we obtain the following:

#### Table No.5

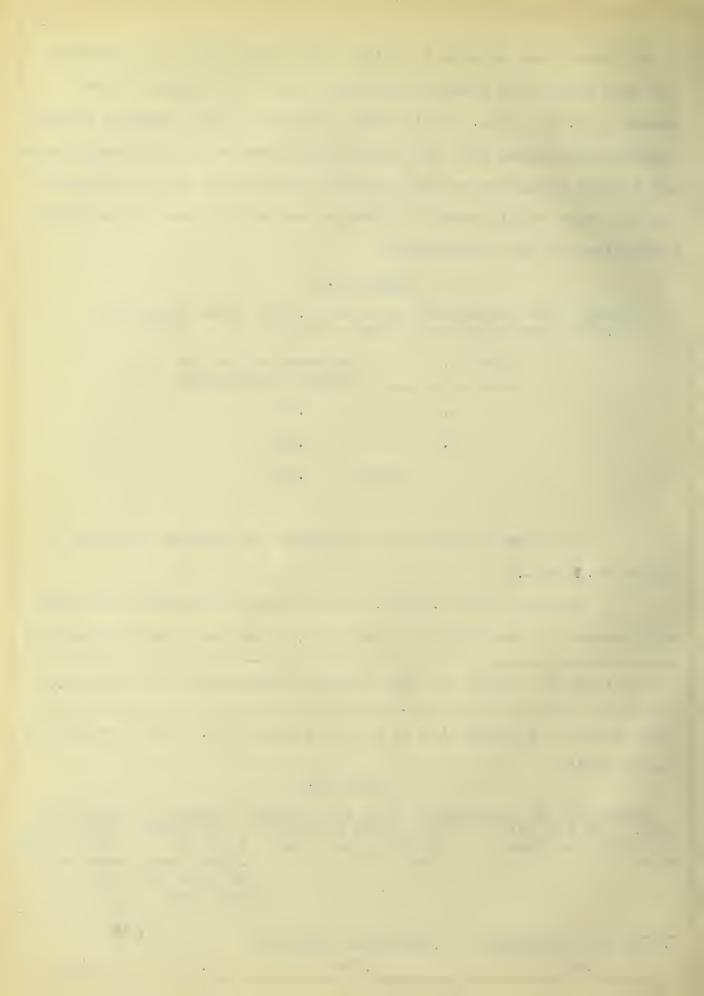
Comparison of Tempera			
Temp. Rise corrected	Temp. Rise correcte	ed Calculated	Difference
for KClO3 and fuse	for KClO3 and fuse	Rise for	between indi-
wire	wire	0.5000 grams	cated and
		from rise for	calculated
		0.7500 gram	rise for
			diff.quanti-
			ty
0.7500 gram C6H5C02Na	0.5000 gram C <sub>6</sub> H <sub>5</sub> CO	Na	

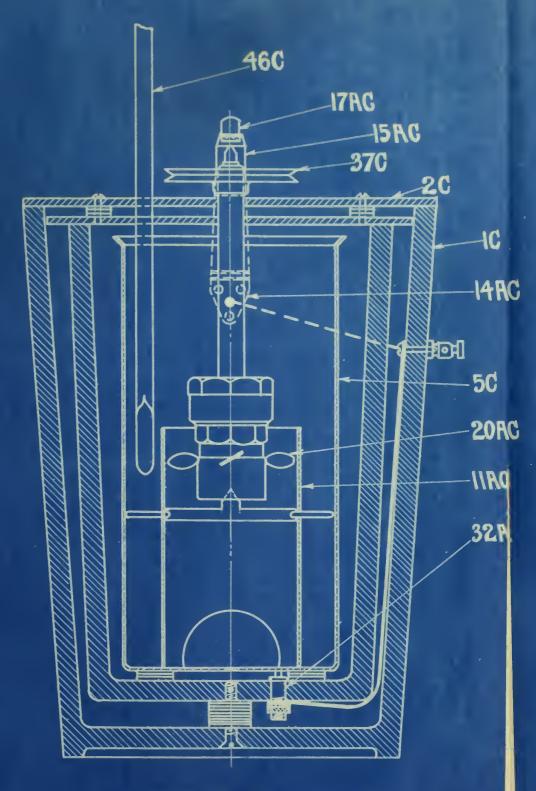
1.730

1.734

0.004

2.602





AC CALORIMETER

58C 5RC 27RC 6RC 2RC 7AC

OMB

200 - 014 of the col-

These results, on account of their uniformity both with the same and with varying quantities of the sodium benzoate, may be considered as constant in behavior thruout the reactions involved. It was adopted, therefore, as the substance used in all subsequent determinations connected with this investigation.

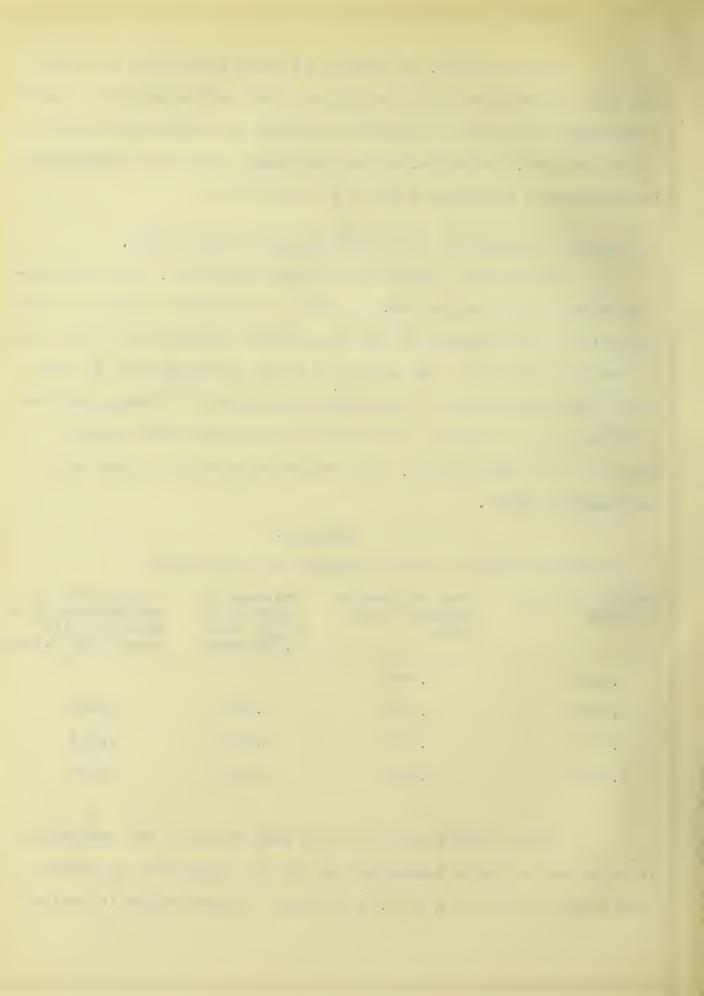
# A Study of the Function of the KC103 and the Heat Value.

Having thus chosen the standard substance, the next question which confronted us was: (a) What is the heat correction to be applied for the reaction of the accelerator (KClO<sub>3</sub>) and (b) How does it react in the bomb? The second of these questions will be left for a later discussion. To determine the first of these questions a series of calorimetric determinations was made using varying amounts of the accelerator, the results of which are given in the accompanying table.

Showing Rises for various Amounts of Accelerator

Amounts of KClO3 in grams	Heat evolved in degrees centi-grade	Increase in amounts of KC10z over 0.500 gram	Increase in temperature rises above the increase for 0.500g.
0.5000	2.627		
0.7500	2.675	0.2500	0.048
1.0000	2.756	0.5000	0.129
1.2500	2.812	0.7500	0.185

These results show that the heat value of the accelerator is more than a simple decomposition for the heat value in passing from KClO<sub>3</sub> to KCl + 3 O is 9.79 calories for gram molecule equiva-



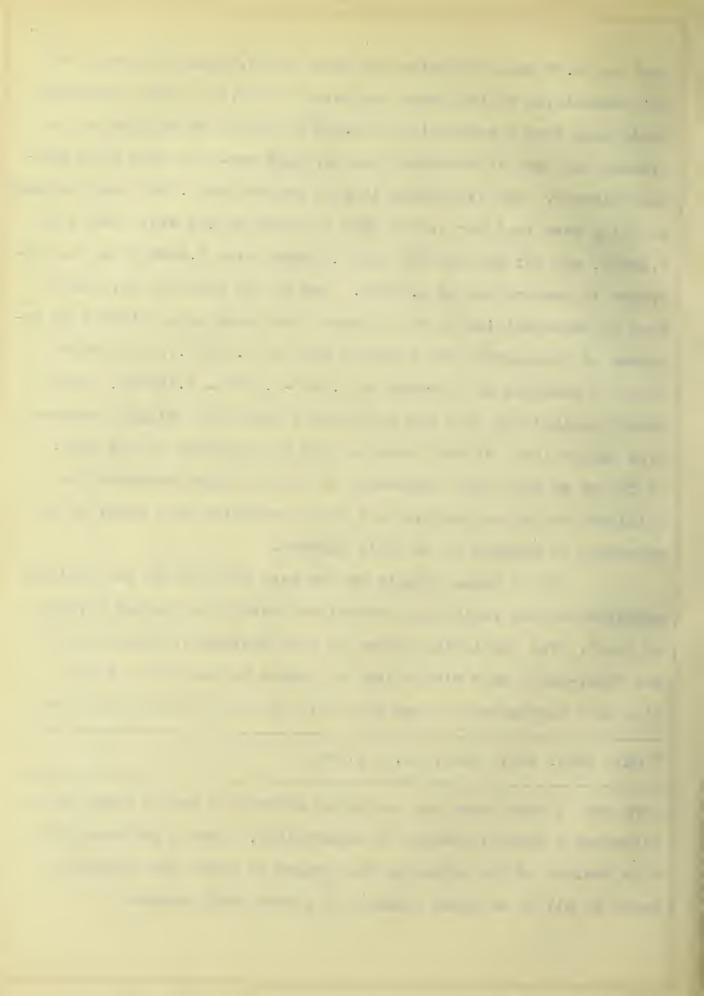
lent to 79.85 small calories per gram, or 39.93 per 1/2 gram, and this calculated to the water equivalent (2123.3) of the instrument would mean that a correction of 0.019°C. should be applied to represent the heat of decomposition for each one-half gram of potassium chlorate. The difference in heat evolved by 0.7500 gram increase of KClOz over that for 0.5000 gfam as shown by the above table is 0.185°C, and for one-quarter gram increase over 0.5000 gram, the increase in temperature is 0.048°C. Now if the reaction were only that of decomposition of the chlorate, we would have obtained an increase of temperature for one-half gram of 0.019°C. but instead there is obtained an increase of 0.185°-0.048° = 0.137°C., which shows conclusively that the accelerator aside from simple decomposition enters into further reaction with the contents of the bomb. To follow up this heat component, it was of course necessary to eliminate so far as possible all other variables that might be of uncertain or unknown as to their amounts.

All of these results so far were obtained in the ordinary peroxide and the radiation corrections made by the method devised by Lord\*. The insulating devise in this instrument consisted of two fiber-board cans with a dead air space between them. Fig.2.

With this arrangement it was difficult to keep the conditions uni-

<sup>\*</sup> Ohio Geol. Surv. Bull. No.9. p.321.

form and in some cases the radiation correction was so large as to introduce a possible source of uncertainty, hence a refinement of this feature of the apparatus was sought in which the radiation would be nil or at least reduced to a very small amount.



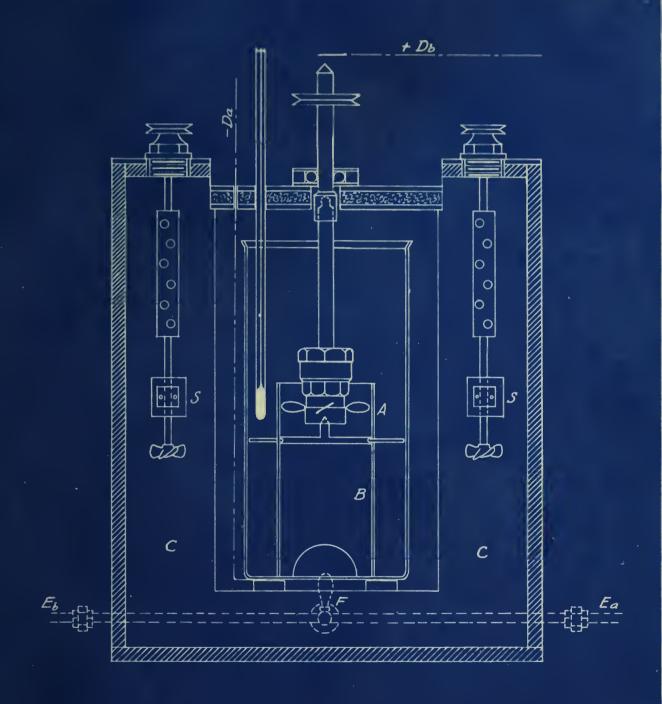


FIG. 3

SECTION THROUGH ADIABATIC CALORIMETER

Books Browns ...

### Changes in the Apparatus.

In order to obviate these difficulties, an adiabatic form of instrument devised by Professor Parr was substituted for the one heretofore used. A cross section of this instrument is shown in the accompanying diagram. Fig. 3.

This instrument consists of a copper vessel A and the support B for the bomb, the same as used in the ordinary calorimeter. These are surrounded by a hollow vessel C which is provided with two stirrers S, one creating an ascending and the other a decending current of water. This hollow vessel is supplied with hot or cold water Ea and Eb. With this arrangement, it is easy to keep the temperature of the outer vessel equal to that of the inner so that the radiation is negligable. The ignition is made by means of the wire Da, which forms a connection with the bomb through the can, and the wire Db, which is held on the top of the bomb. Both the inner and outer vessels are provided with Beckman thermometers standardized by the Bureau of Standards.

# Additional Determinations varying the Amounts of Aceelerator.

A series of calorimetric determinations similar to those previously described, i.e., using a constant amount of sodium benzoate and varying amounts of potassium chlorate, was made, the results of which are given in the accompanying table.

# Table No.7

Showing Rises in degrees centigrade for varying amounts of accelerator with 0.7500 gram  ${\rm C_{6}H_{5}CO_{2}Na}$  including fuse wire.

0.5000 gram KC103	0.7500 gram KC103	1.0000 gram KC103	1.2500 gram KC103
2.639	2.715	2.761	2.837
2.631	2.715	2.764	2.845



m.	able	MO	77	100	nti	nua	a V
110	an Te	IN O	. (		11 6 7	Hua	u. /

	2.643	2.709	2.778	2.833
	2.631	2.700	2.784	2.838
	2.630	2.710	2.785	2.849
	2.631	2.702	2.777	2.841
	2.640	2.703	2.763	2.834
	2.633	2.712	2.770	2.845
	2.635	2.707	2.774	2.832
	2.645	2.704		2.839
	2.644	2.704		2.838
Av.	2.637°C.	2.707°C.	2.773°C.	2.839°C.

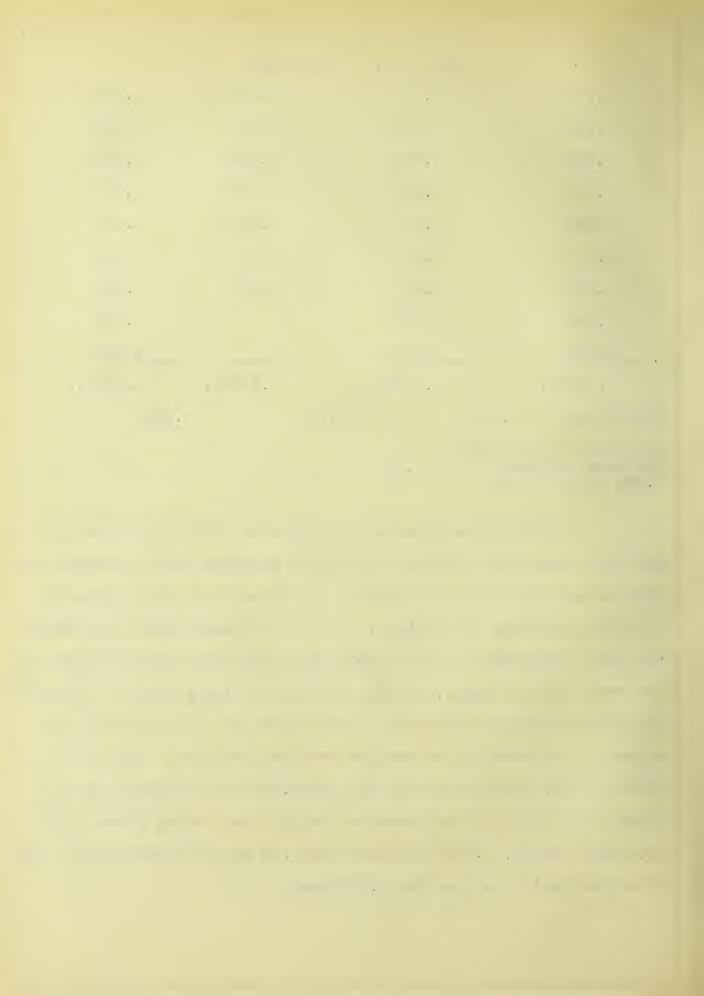
Differences 0.070

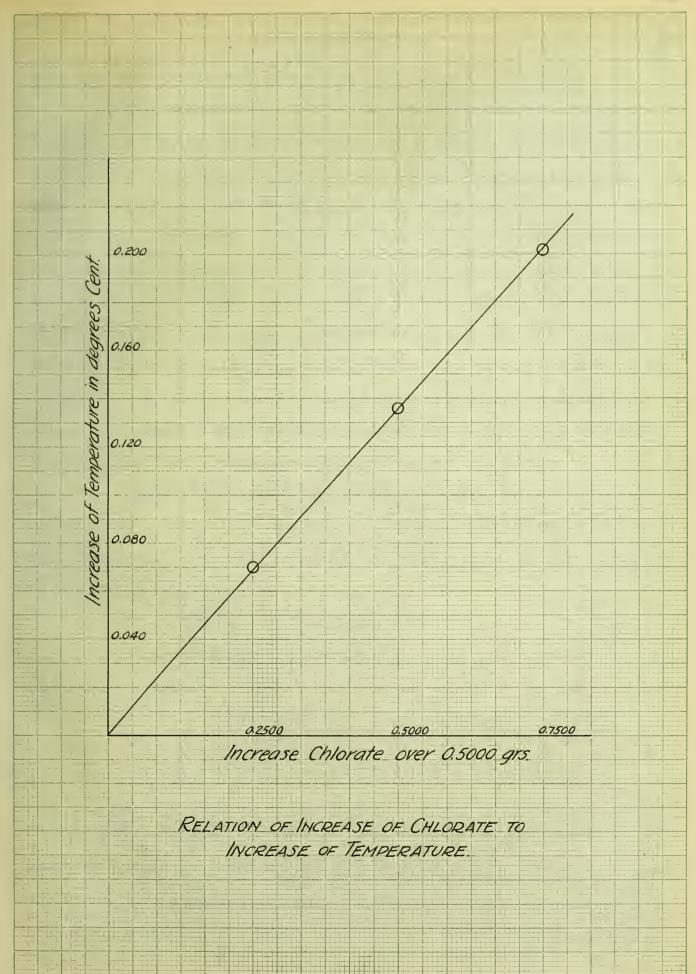
0.066

0.066

Average of differences) for each increase of ) 0.067 0.250 gram of KClO3 )

Plotting the increase of potassium chlorate as abscissa and the temperature increase, over that produced by the charge containing one-half gram of chlorate, as ordinate the curve given on the following page is obtained. It is to be noted that this curve has been constructed on the theory that there are two reactions for of the accelerator; namely, (a) The reaction taking place for the amounty chlorate from zero to one-half gram and (b) The reaction for the chlorate from one-half to one and one-quarter grams. The curve shows on this hypothesis that the temperature differences are in direct proportion to the amount of accelerator taking place in the reaction; namely, 0.067° rise for each .25 gram of chlorate over and above the basic reaction for 0.500 gram.





Don'T LIF (LC V)

Reaction for the first one-half gram of Potassium Chlorate.

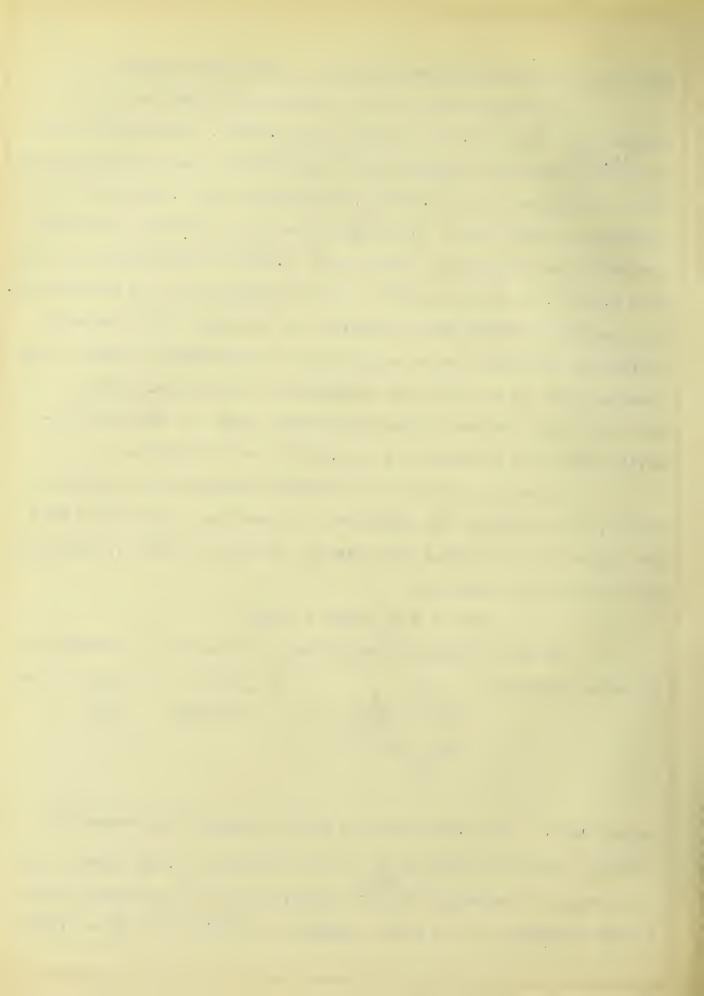
The average rise for the charge containing one gram of accelerator (Table No.7) is found to be 2.773°C. Subtracting the (p.10) correction/heretofore adopted for the accelerator not including fuse wire of .150°C we obtain 2.623°C., as the rise for 0.750 gram sodium benzoate and fuse wire. Taking the rise for the charge containing one-half gram of chlorate (Table No.7) 2.637°C. and subtracting from this 2.623°C. we obtain 0.014°C., the correction for the accelerator. This correction would seem to warrant us in saying that the heat correction for the first one-half gram of accelerator is due to the decomposition of the chlorate according to the equation KClO3 = KCl + 3 O since we have stated previously (page 11) that this reaction calls for a correction of 0.019°C. per half gram.

Since the hydrogen of the sodium benzoate is easily oxidized, it is assumed for purposes of theoretical calculation that the oxygen thus liberated oxidizes the hydrogen to water, according to the following equation:

 $KC10_3 + 3 H_2 = KC1 + 3 H_20$ 

On this assumption the hydrogen available for combustion in sodium benzoate H is 5 H = 5 of the HC C-C-No.  $C_{6}H_{5}CO_{2}Na$  144

amount used. With 0.7500 gram of sodium benzoate the amount of hydrogen available would be  $\frac{5}{144}$  of this amount or 0.026 grams. Now the amount of potassium chlorate required for this quantity of hydrogen according to the above equation is  $\frac{122.6}{142.6} \times 0.026 = 0.5313$ 



gram. The heat of decomposition for this amount of chlorate calls for a correction of 0.020°C. and as shown in the foregoing discussion the first one-half gram of chlorate has been given a correction of 0.019°C. These two temperatures show sufficient agreement to indicate that the above hypothetical assumption indicates at least in a general way the direction taken by the various reactions involved. There must be recognized, however, that other secondary reactions take place, but it must be evident from these calculations that they are without appreciable effect so far as modifying the final result is concerned.

### Reaction for the Potassium Chlorate in excess of one-half gram.

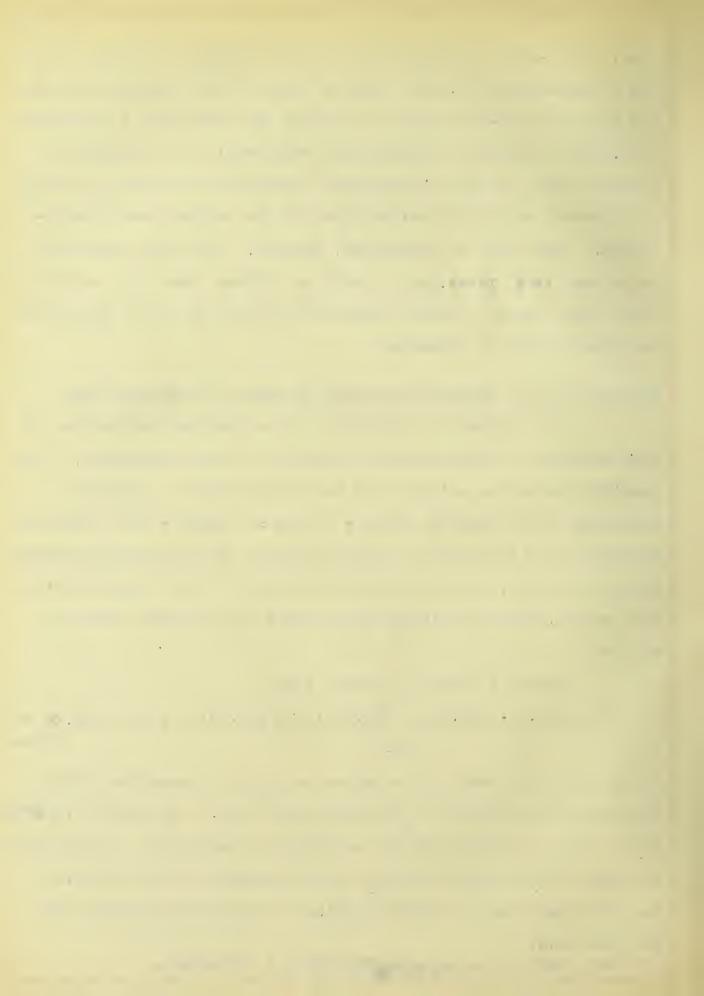
In studying the conditions for a possible explanation of this increase for the secondary reaction for the accelerator, it is possibly due to the oxidation of the sodium oxide to peroxide according to the equation  $KClO_3 + 3 Na_2O = 3 Na_2O_2 + KCl$ . This is warranted from the fact that  $Na_2O$  is formed in the reaction between  $Na_2O_2$  and carbon, and this  $Na_2O$  at a red heat would recombine with free oxygen.\* Now by calculating the heat of the above reaction we have -

 $KC10_3 + 3 Na_20 = 3 Na_20_2 + KC1$   $(3 \times 119.8 + 105.65) - (95.86 + 3 \times 100.26) \times 1000 = 558.0 \text{ calories.}$ 

By dividing this number of calories per gram of potassium chlorate by the water equivalent of the apparatus (2123.3) we obtain 0.2628°C. as the rise in temperature for one gram of accelerator. Calculating the temperature corrections for various amounts of chlorate over one-half gram from the above reaction we obtain the results shown in Table No.8.

\* Also, there is no gas pressure after a combustion.

122.6



### Table No.8

Comparison of calculated temperatures and the differences given in Table No.7 for the Potassium Chlorate over one-half gram.

	0.7500 gram KClO <sub>3</sub> (0.5000+0.2500)	1.0000 gram KC1( (0.5000+0.5000)	03 1.2500 gram KClO3 (0.5000+0.7500)
Calculated	0.0657	0.1314	0.1971
Experimental Table No.7	0.0700	0.1360	0.2020
Difference	0.0043	0.0046	0.0049

Since these results so nearly agree it would appear that the following equations represent the reactions taking place in the bomb due to the presence of the potassium chlorate:

- (a) For the first one-half gram of potassium chlorate
  - $KC10_3 = KC1 + 30$
- (b) For the potassium chlorate over one-half gram including both decomposition and recombination for the excess KClO<sub>3</sub> + 3 Na<sub>2</sub>O<sub>2</sub> = 3 Na<sub>2</sub>O<sub>2</sub> + KCl

NOTE: The calculated value for 1 gram = rise of 0.2628°C.

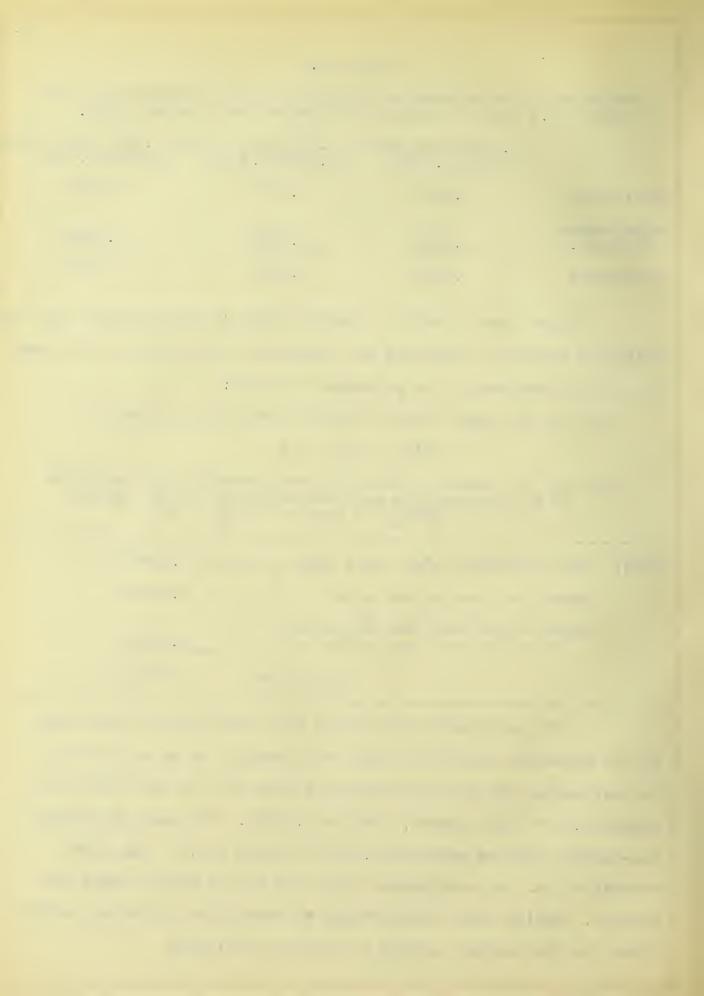
Hence. for one-quarter gram = " 0.06570

Compare this with the determined value average one-quarter gr. = 0.0673

Difference 0.0016

The components parts which go to make up the heat value of the potassium chlorate we may then conceive to be as follows:

The correction for the first one-half gram will be the heat of decomposition of this amount, that is 0.019°C. For each succeeding one-quarter gram we must add 0.067°C. (Table No.7). The total correction for the accelerator will then be the sum of these two amounts. Making these calculations we obtain the following corrections for the various amounts of potassium chlorate.



### Table No.9

Correction for the various amounts of accelerator

Adding to these corrections 0.003°C. for the heat of the fuse wire and subtracting this total correction from the average results given in Table No.7 we obtain the following heat values for the sodium benzoate only.

### Table No.10

Showing the average heat values from Table No.7 for 0.75 gr. sodium benzoate with correction applied for successive increments of KClO<sub>3</sub>.

	0.5000 gr. KClO <sub>3</sub>	0.7500 gr. KClo <sub>3</sub>	1.0000 gr. KC103	1.2500 gr. KC103
From Table No.7 average tempera- tures	2.637	2.707	2.773	2.839
Total corrections	0.022	0.089	0.156	0.223
Heat value for the sodium benzoate (.75 gr)	2.615	2.618	2.617	2,616

Average temperature for 0.7500 gram sodium benzoate 2.6185°C.

It remains now to calculate this average rise of 2.6185° for 0.75 gram of sodium benzoate to calories. The process is as follows:

The water used (2000 grams) plus the water equivalent of the metal parts amounts to 2123.3 grams. As previously stated seventy-three per cent of the total heat evolved is due to the combustible substance and twenty-seven per cent to the heat of combination of the carbon dioxide and water with the sodium oxide. Then

- The state of the

THE RESERVE THE PARTY NAMED IN

YEN.

.

\*O 4.00 - Fra

The disk of the last tool to the same of t

All place property

.

The second section of the section of the

THE RESIDENCE OF THE PARTY OF T

1.

0.75 × 2123.3 × 2.6185 
0.7500 

zoate. In this calculation no account is taken of the oxygen compounds of the material, that is the hydroxyl and carbonyl constituent which would generate heat in reaction with the sodium peroxide. The value of the heat increments due to the hydroxyl and carbonyl radicles in reaction with the sodium peroxide would, therefore, be represented by the difference between the value as above derived and the accepted value for the combustion of sodium benzoate. In the absence of such values we are obliged to make a determination using the accepted standard; namely, the combustion in an oxygen calorimeter.

# Heat Value of Sodium Benzoate using the Oxygen Calorimeter.

In carrying out the combustion in the oxygen calorimeter we are able, by using the necessary precautions, to obtain complete combustion of the sodium benzoate, but three other reactions took place; namely, (a) the heat of formation of the nitric acid (which is always an impurity in commercial oxygen, (b) the heat of solution of the sodium carbonate formed, and (c) the heat of neutralization of the nitric acid and sodium carbonate.

The amount of nitric acid formed was determined in the following manner: From the amount of sodium benzoate used we calculated the sodium carbonate formed. The washings from the bomb were titrated for the alkaline content; the difference between these two quantities being the quantity of sodium carbonate used in neutralizing the sodium carbonate which was formed. The heat of combustion of one gram of nitrogen is 1020 calories and as 106 grams of sodium carbonate is equal to 28 grams of nitrogen, one gram of

The same of the sa The state of the s 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 the state of the s 

sodium carbonate is equal to 269.4 calories when referred to the combustion of nitrogen.

In the heat of neutralization one gram of sodium carbonate is equal to 67.7 calories. The heat of solution is negligable.

An example may make these calculations clearer:

Weight of sodium benzoate ----- 1.0001 grams

Calculated to sodium carbonate --- 0.3680 "

Acidity calculated to Na2CO3 ---- 0.3344 "

Nitric acid calculated to  $Na_2CO_3 \cdot 3680 - .3344 = 0.0336$ 

#### Corrections -

Heat of formation of HNO3 0.0336 x 269.4 = 9.05 calories

Heat of neutralization .0336 x 67.7 = 2.27 "
Total corrections ------ 11.32

Total indicated calories per gram ---- 5282.02

Total corrections ----- 11.32

Heat of combustion of one gram of sodium benzoate only ---- 5260.70

The heat of combustion of the sodium henzoate as thus determined with the oxygen calorimeter, with the above corrections applied, is shown in the following table.

# Table No.11

Heats of combustion of sodium benzoate in the oxygen calorimeter

Test No.	Calories per gram
1.	5260.7
2.	5270.8
3.	5272.2
4.	5266.6
Average	5267.6

A CONTRACT OF THE PARTY OF THE I are a light took and the light A CONTRACTOR OF THE PROPERTY O - 15 15 16 19 11411 and the second second second second second • .

The difference between the heat of combustion 5411.5 - 5267.7 = 143.8 calories is due to the reaction of the hydroxyl and carbonyl group with the sodium peroxide and has heretofore been called the hydration factor. Dividing this amount (143.8) by the water equivalent of the instrument we obtain 0.0677°C. as the correction to be applied for the hydration factor of each gram of sodium benzoate, or 0.0508 for 0.75 gram - the standard amount which is most suitable for combustion in the apparatus.

. The same of the same

#### SUMMARY

- 1. Sodium benzoate possesses the necessary properties for a standard combustible substance to be used in the peroxide calorimeter. Of the substances examined, this was found to be the most desirable.
- 2. The heat value of the potassium chlorate is more than a simple decomposition.
- 3. The equations representing the reactions for the potassium chlorate are as follows:
  - (a) For the first one-half gram

$$KC10_3 = KC1 + 3 0$$

(b) For the excess over this amount

$$KC10_3 + 3 Na_2 0 = 3 Na_2 0_2 + KC1$$

- 4. The correction to be applied for the first one-half gram of accelerator is 0.019°C. and for each succeeding one-quarter gram is 0.067°C.
- 5. The hydration factor for the sodium benzoate is 0.0677°C. per gram, or 0.0508°C. for 0.75 gram the standard amount of material found most suitable for reaction in the apparatus.





